



Volatile Losses from Exposed Sediment

PURPOSE: This technical note describes laboratory investigations conducted to obtain flux data for the emission of volatile organic chemicals (VOCs) from sediment exposed to atmosphere. These investigations are being used to develop and validate predictive volatile emissions models. Laboratory experimental techniques and results obtained during these investigations are described.

BACKGROUND: Contaminated sediments and dredged materials are potential sources of volatile compound emissions, many of which exist in high concentration in these materials. The loss of volatile contaminants from dredged sediments is an environmental problem that is receiving increasing attention.

Previous laboratory investigations conducted at the U.S. Army Engineer Waterways Experiment Station (WES) with New Bedford Harbor, Massachusetts, sediment showed large amounts of VOCs emitted when the material was disturbed and exposed to air. The factors affecting volatile losses are largely unknown. Dredging and storage operations in confined disposal facilities (CDFs) can increase the opportunity for VOC emissions. Methods for predicting volatile losses from sediments during different aspects of dredging and disposal operations are needed to develop guidelines for controlling possible contaminant volatile emissions. Presently, neither field data nor models exist to accurately predict VOC emissions from sediments under different environmental and operational conditions.

INTRODUCTION: Dredging and disposal of contaminated sediments can pose significant environmental problems. During dredging operations and storage of sediments in CDFs, there is increased opportunity for VOCs to be emitted from contaminated dredged materials. Exposed sediments are a primary volatile contaminant pathway (Figure 1). In a CDF, sediments undergo cyclic "wet/dry" conditions, variations in the relative humidity of the air above the sediment, and temperature fluctuations. Moisture content has also been shown to affect the sorptive capacity of sediments for VOCs (Valsaraj and Thibodeaux 1988).

Mathematical models have been proposed to estimate the air emission rates of various volatile organic compounds from sediments (Thibodeaux 1989). These models are currently being tested using data generated at the WES Environmental Laboratory and the Louisiana State University (LSU) Department of Chemical Engineering, in laboratory investigations using both laboratory spiked and field sediments. Laboratory procedures developed at the WES, in coordination with LSU, were used in all experiments (Price and others 1996).

MATERIALS AND METHODS:

- **Sediment.** Two sediments were used in the experiments described here. The first sediment was obtained from University Lake (UL) in Baton Rouge, LA. Two separate experiments

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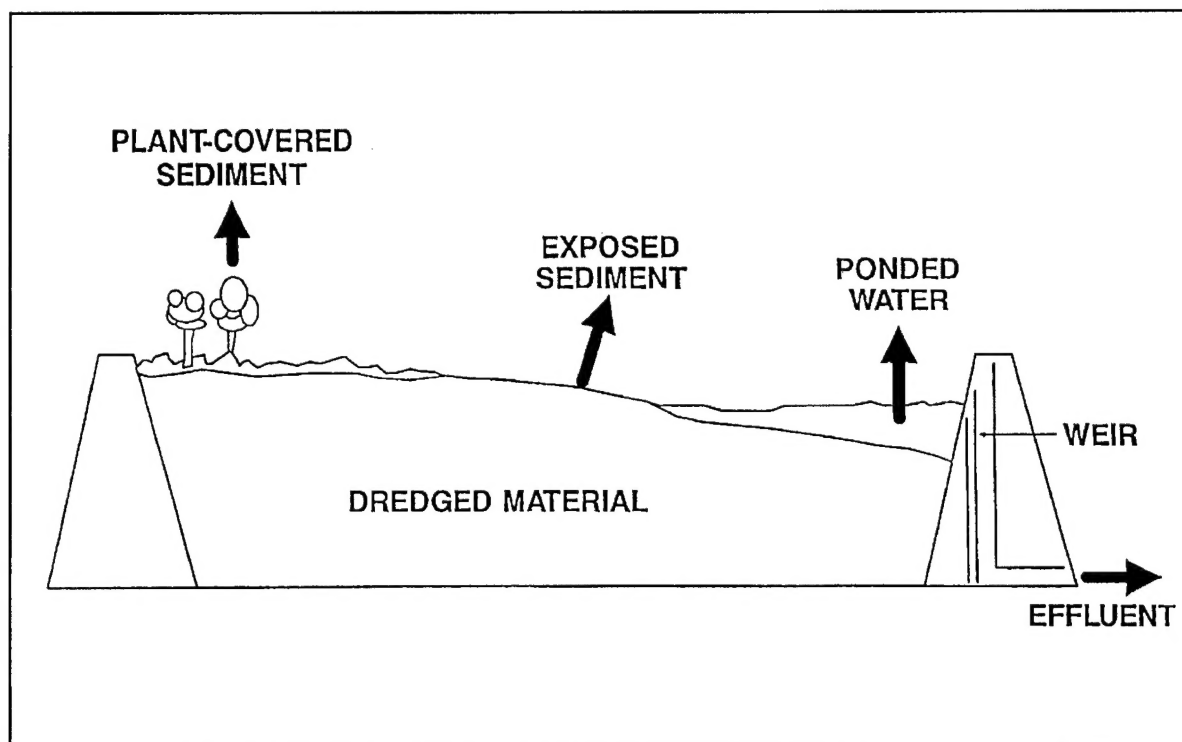


Figure 1. Pathways for release of volatile emissions from dredged material

were conducted with UL sediment to determine polycyclic aromatic hydrocarbon (PAH) flux from sediments with initial moisture contents of 48 and 25 percent. The sediment was spiked with three PAHs: pyrene, phenanthrene, and dibenzofuran. Testing and analysis of UL sediment was conducted at LSU. The second sediment investigated was contaminated sediment obtained from Indiana Harbor Canal (IHC). This sediment contained several organic contaminants, including PAHs, polychlorinated biphenyls (PCBs), and inorganic compounds of concern, such as ammonia and hydrogen sulfide. The IHC sediment contains 0.9 percent oil and grease. Volatile emission testing for PAHs, total recoverable petroleum hydrocarbons (TRPHs), PCBs, ammonia, and hydrogen sulfide was conducted with the IHC sediment at WES for the Corps' Chicago District. For experimental purposes and model validation, only three PAH compounds were evaluated for emission comparisons between the two sediments. PAHs were chosen as representative VOCs due to their prevalence in contaminated sediments. The physical and chemical properties of both sediments are summarized in Table 1.

- **Flux chambers.** All tests were conducted using VOC flux chambers designed by LSU and constructed at WES and LSU (Figure 2). The two-piece anodized aluminum chambers were devised to hold sediment at a depth of 10 cm with a surface area of 375 cm². The top portion of the flux chamber was designed with channels to distribute airflow uniformly across the sediment surface. The chambers were sealed with an O-ring and threaded fasteners for an airtight fit.

Table 1. Physical and Chemical Properties of Sediments¹

Property	University Lake		Indiana Harbor
	High Moisture	Low Moisture	
Percent sand	3	3	45
Percent silt	41	41	46
Percent clay	56	56	8
Percent total organic carbon	4	4	2.6
Percent oil and grease	NA	NA	0.9
Porosity	0.7	0.44	0.79
Bulk density, g/cm ³	0.67	1.7	0.6
Percent initial moisture (w/w)	48	25	54
Dibenzofuran, mg/kg	66	108	NA
Naphthalene, mg/kg	NA	NA	38
Phenanthrene, mg/kg	65	97	51
Pyrene, mg/kg	69	94	59
Total recoverable petroleum hydrocarbons, mg/kg	NA	NA	12,790

¹ Data obtained from Ravikrishna and others (in review).

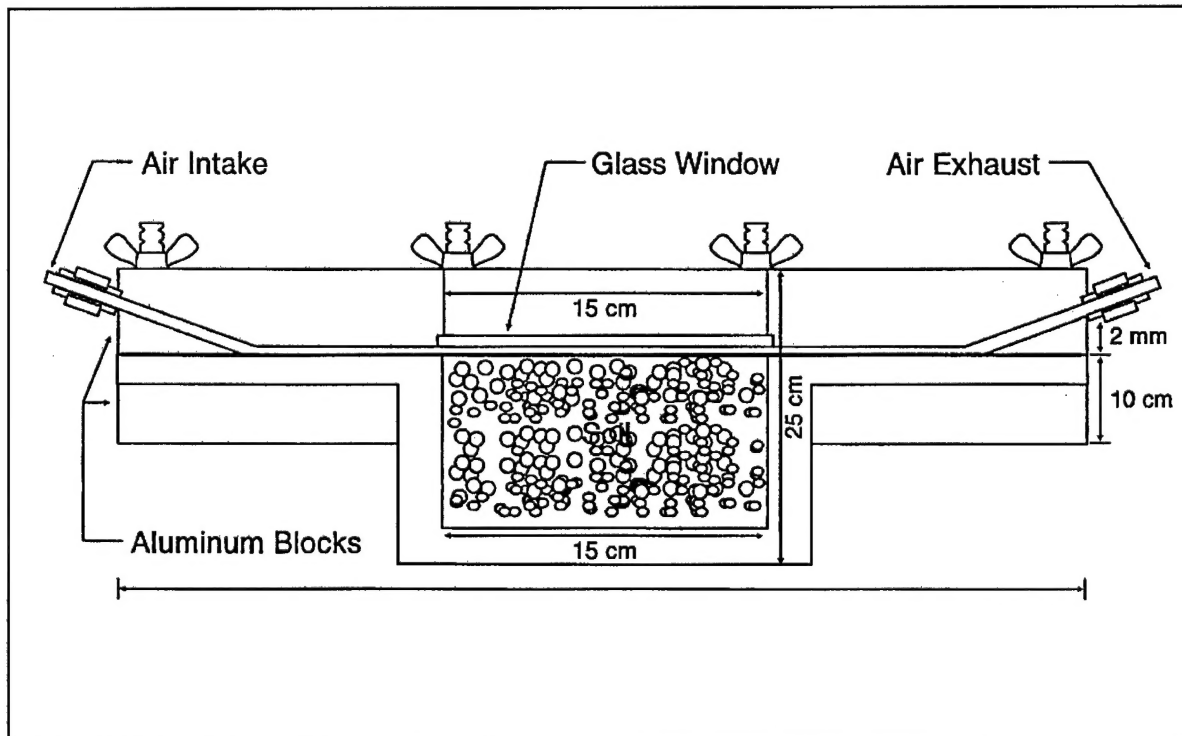


Figure 2. Schematic of volatile test chamber

Contaminant-specific adsorbent-filled air sampling traps were attached to the chamber exit ports. PAHs/TRPHs and PCBs were trapped on XAD-2 resin enclosed in glass sample tubes (Orbo 44 from Supelco, Inc.). Traps were removed from the exit lines at the end of each sampling interval. Solvent was extracted and analyzed according to EPA method 8270 for PAHs/TRPHs and method 8081 for PCBs (U.S. Environmental Protection Agency 1982).

Contaminant flux, $N(t)$, through the chambers was calculated using the equation

$$N(t) = \frac{\Delta m}{\Delta t A_c}$$

where

Δm = mass (ng) of compound collected on the trap in time Δt (hr)

A_c = area of the sediment-air interface, cm^2

EXPERIMENTAL DESIGN: Flux chambers were filled with a known amount of homogenized sediment (wet weight) and sealed. Air was passed over the sediment surface at 1.7 L/min, and relative humidity was maintained by using an in-line bubble trap as needed to add moisture vapor. A thermohygrometer (Cole-Parmer) was connected to the exit port to monitor air temperature and relative humidity.

Experiments with IHC sediment were conducted to provide information on maximum contaminant fluxes expected under different air humidity, sediment moisture, and site management conditions that might occur during CDF operations. The sampling schedule consisted of five continuous runs simulating various environmental and operational scenarios.

Runs I and II gave maximum initial contaminant fluxes from wet sediment under dry and humid air conditions. In Run I, dry air was passed over the sediment surface for 2 weeks, after which the relative humidity of the air was increased to 98 percent and samples were taken over a 7-day period (Run II). Run III simulated a rainfall event in which the sediment was rewet to near field capacity and dry air was passed over the sediment surface for 14 days. Run IV represented the occurrence of mechanical mixing during CDF operations. The sediment was reworked in the chambers in glove bags equipped with sampling tubes to trap contaminants released during mixing. Dry air was then passed over the sediment for 7 days. The sediment was again rewet to near field capacity for Run V, and dry air was again passed over the sediment surface for a final 7 days. Air samples were taken as follows:

Run I	6, 24, 72, 168, 240, and 336 hr
Run II	6, 24, 72, and 168 hr
Run III	6, 24, 72, 168, 240, and 336 hr
Run IV	6, 24, 72, and 168 hr
Run V	6, 24, 72, and 168 hr

Testing of UL sediment conducted at LSU was designed to formulate comparisons of contaminant fluxes between a laboratory-spiked sediment and a naturally contaminated sediment. Experimental procedures were designed to determine the effects of changes in moisture content and relative air humidity on PAH emissions from each sediment (Ravikrishna and others, in press).

RESULTS:¹

- **Moisture fluxes.** Moisture fluxes were monitored during the course of all experiments. Water flux from the higher moisture UL sediment decreased from 0.006 to 0.005 g/cm²•hr in 48 hr and remained relatively constant for the duration of the test. Moisture content of the surface sediment and underlying layers did not vary significantly, indicating that the sediment surface remained relatively "wet" over the course of the test. Water flux from the lower moisture UL sediment was similar to that from the higher moisture sediment, but did decrease significantly after 400 hr. The water flux from the Indiana Harbor sediment remained at 0.005 g/cm²•hr throughout the experiment, with no difference between final surface and underlying sediment moisture contents.
- **Contaminant fluxes.** Experiments conducted with UL sediment were designed to determine and form comparisons of maximum initial contaminant fluxes from University Lake and Indiana Harbor sediments. The effects of different initial sediment moisture contents and relative air humidity conditions on PAH emissions were investigated.

For experiments conducted with UL sediment, dry air (0 percent relative humidity) was passed over the sediment surface for 568 hr. Within the first 48 hr of the experiment, dibenzofuran fluxes decreased from 32 to 12 ng/cm²•hr and from 111 to 10 ng/cm²•hr in the high- and low-moisture content UL sediment, respectively. During the first 48 hr, phenanthrene fluxes decreased from 7 to 3.5 ng/cm²•hr and from 13 to 3 ng/cm²•hr. Even though no decrease in sediment moisture flux or overall sediment moisture occurred in experiments run with IHC sediment, PAH fluxes sharply decreased within 168 hr after applying "dry" air over the sediment surface (Figure 3). This phenomenon may be due to the formation of a thin oil-film layer on the sediment surface, which would evaporate quickly resulting in the observed decline in flux (Ravikrishna and others, in press). Subsequent diffusion of contaminants from the sediment to the air would be significantly slower through the oil and grease within the sediment. Pyrene fluxes remained relatively constant throughout all experiments with both sediments. This trend is in contrast to earlier investigations, where fluxes decreased significantly in conjunction with sediment surface drying decreasing the sediment sorptive capacity or retardation factor (R_f) (Valsaraj and others 1997).

In experiments conducted with UL sediment, the relative humidity of the air was increased to 90 percent after 568 hr. No discernible increase in PAH fluxes was noted in the experiment

1 Results reported herein summarize findings found in Ravikrishna and others (in press).

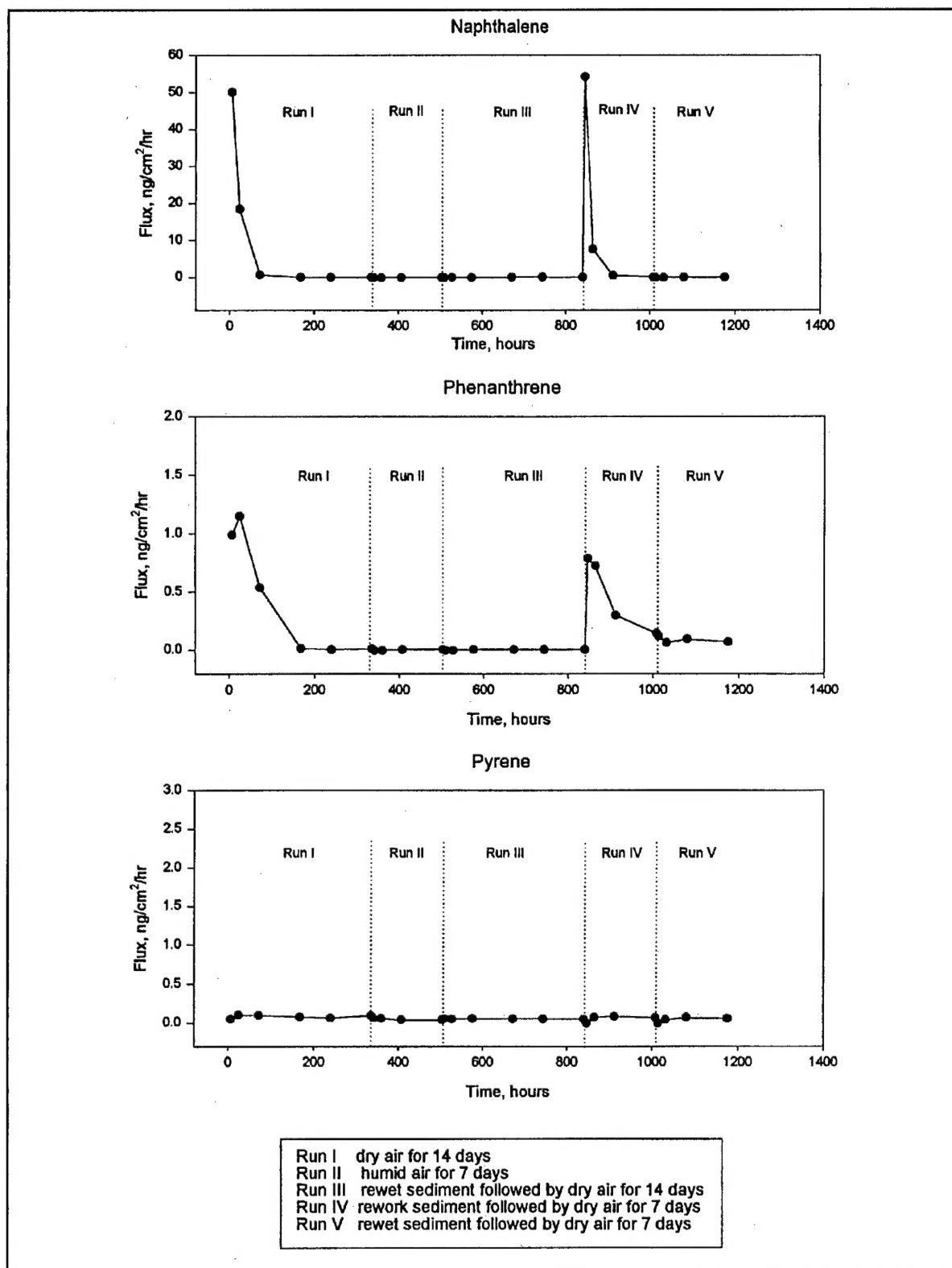


Figure 3. PAH fluxes from Indiana Harbor Canal sediment

conducted with the higher moisture content UL sediment. If the sediment surface was "dry," a noticeable increase in contaminant flux would have occurred. Although the water flux from the lower moisture UL sediment remained relatively constant during the first 400 hr of the test, a noticeable "drying front" formed on the sediment surface at the air inlet and progressed toward the exit port for the remainder of the experiment. In contrast to the higher moisture UL sediment, an increase in PAH flux rates occurred when the relative humidity of the air was increased. Dibenzofuran and phenanthrene fluxes increased to 50 and 10 $\text{ng}/\text{cm}^2\cdot\text{hr}$, respectively. An increase in relative air humidity after 336 hr did not result in any increase in PAH flux in the experiment run with IHC sediment. Sediment moisture flux did not change during the course of the test, which would account for the lack of an increase in PAH emissions. An increase in flux rates observed at test Run IV was possibly due to the formation and subsequent evaporation of another sediment surface oil-film layer during reworking of the sediment (Figure 3).

Ravikrishna and others (in press) found the predicted values for phenanthrene in good agreement with experimental values for the UL sediments, but the IHC sediment model predictions were orders of magnitude larger than for observed fluxes (Figure 4). Measured fluxes from the IHC sediment were lower than those from UL sediment. This suggests that a smaller concentration of phenanthrene was available for diffusion, probably due to irreversible binding through sediment aging involving sediment sorption and partitioning processes (Fu, Kan, and Tomson 1994; Kan, Fu, and Tomson 1994; Kan and others 1997).

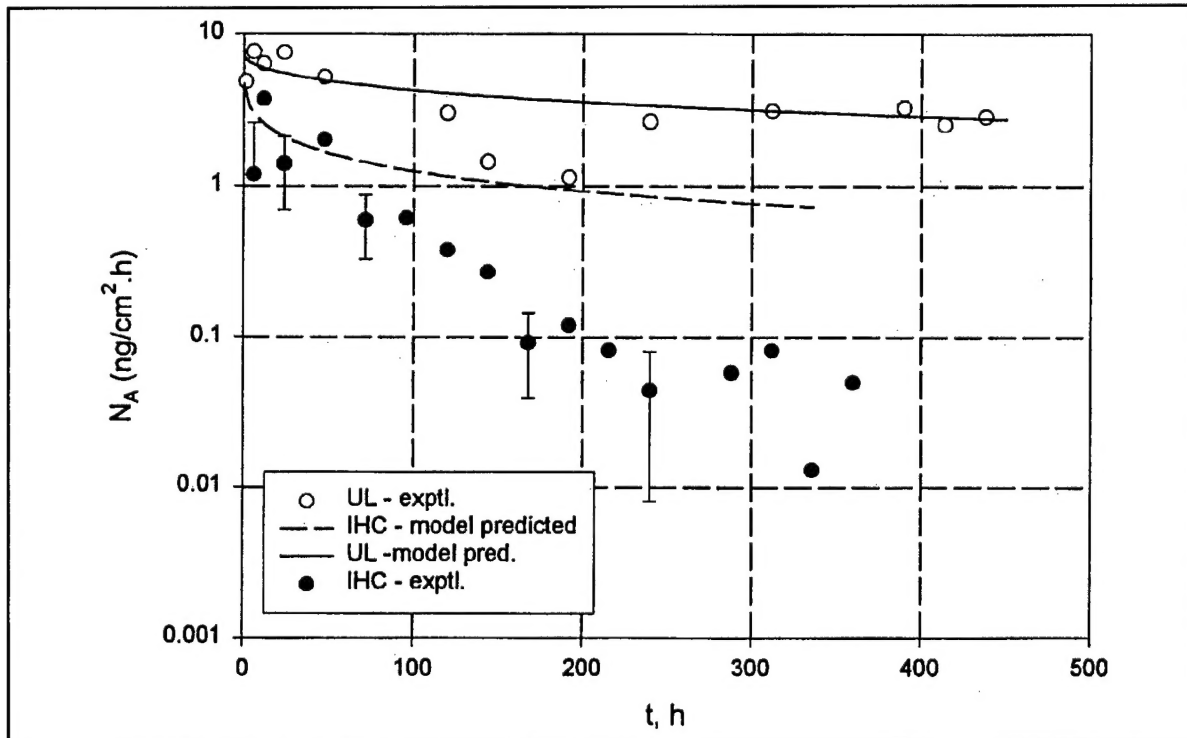


Figure 4. Comparison of dibenzofuran flux from University Lake (UL) and Indiana Harbor canal (IHC) sediments

CONCLUSIONS: Results indicate that VOC fluxes depend upon several factors. Relative humidity can possibly affect flux rates, but its influence depends upon moisture content and sediment physical and chemical characteristics. Measured fluxes for Indiana Harbor sediment were orders of magnitude lower than model predictions and laboratory data collected in a comparable study conducted with laboratory spiked sediment (Valsaraj and others 1997). Sediment physical and chemical characteristics, such as contaminant aging, porosity, and percent oil and grease, probably decreased fluxes.

Comparison of the behavior of the IHC sediment to the laboratory-spiked UL sediment revealed important implications for estimating PAH air emission fluxes. PAH emissions can be overestimated if models developed through calibrations obtained from laboratory-inoculated sediments are used to predict fluxes from field-contaminated sediments. LSU is currently pursuing development of appropriate models for aged field-contaminated sediment in coordination with the WES.

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